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**METHOD FOR THE SURFACE TREATMENT OF METAL ARTICLES**

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No Drawing, Filed June 22, 1965, Ser. No. 466,091

Int. Cl. B44d 1/34, 1/36, 1/14

U.S. Cl. 117-49

8 Claims 10

**ABSTRACT OF THE DISCLOSURE**

A method of treating the surfaces of iron-base metal articles, such as steels which rust, which comprises subjecting the articles to the action of a pickling solution containing a mineral acid mixture, a pickling accelerator, a corrosion inhibitor, a wetting agent, and an organic solvent of polar character which is miscible in water and which is a solvent for fats, fatty acids and mineral oils, washing the articles with water after completion of pickling, and finally treating the washed surfaces with a solution containing an organic solvent selected from the group consisting of aliphatic and aromatic hydrocarbons, a wetting agent, a soluble film-forming substance and a drying agent, whereby the finally treated surfaces are characterized by a corrosion-preventing film which may serve as a base for receiving a primer, enamel or other surface coating.

This invention relates to the surface treatment of metal articles in order to provide clean surfaces for further treatment, such as for applying thereon a primer coat, an enamel or other type of coating. In particular, the invention is directed to a simple method for cleaning and treating metal surfaces.

Surface preparation has a direct effect on the performance of a coating, such as a coating of chromate primer, paint, enamel, or other surface coatings employed on metal surfaces. The best coating applied may fail prematurely if applied to a contaminated or improperly prepared surface.

In order to prepare for the undercoating of the surfaces of metallic articles, such as automobile bodies, they must first be treated to remove grease, rust, dirt and the like, and the clean surface passivated prior to applying the coating. Numerous operations have heretofore been required for this purpose, such as alkaline or vapor degreasing, acid pickling, rinsing with water, phosphating, intermediate rinsing with cold and hot water, treatment with demineralized water, chromating, again rinsing with water, drying by heat or with compressed air, etc. Immediately following the cleaning, the undercoat or top coat is applied. If the enamel or lacquer is not applied immediately after the previously customary preliminary treatment, under-corrosion is apt to occur whereby extensive expensive reworking may be required. Generally, the treatments used heretofore were carried out in part at temperatures of up to 120° C. and were usually cumbersome, time-consuming and expensive. The treating steps employed were not always effective, particularly because of the large number of operations involved, this generally being apparent by the occurrence of under-corrosion.

It is the object of the present invention to reduce the number of operations to three basic steps whereby to effect a considerable simplification and reduction in operational cost, while at the same time inhibiting under-corrosion and providing substantial improvement in quality. An important feature of the method is that it can be carried out at room temperature and thus does not require

the application of any heat, because of which considerable reduction in expense can be realized.

Broadly speaking, in the first step of the method, degreasing and rust removal are simultaneously effected, while creating a passivating layer having adhesive properties on the treated surface. In the second step, the rinsing or washing with normal tap water is effected, while in the third step, drying is effected in a single operation by displacement of the water, and passivation then effected by the application of a bond-producing layer which protects the metal against under-corrosion. In contradistinction to the ordinary wash primers, an article such as a vehicle body which has been treated in this manner can be stored in the open for up to a year without corrosion. The layer applied in the third step is of slight thickness, in view of the relatively low solids content of the solution employed and is therefore not the same as a priming coat.

In carrying out the method of the invention, the workpieces are treated in the first step in a solution containing inorganic acids, a pickling accelerator, an inhibitor, an organic solvent which is miscible in every proportion with water, and a wetting agent or wetting agent mixture. Broadly, the composition of the solution comprises the following:

	Percent by weight
Inorganic acids (100%) -----	From about 20 to 35
Pickling accelerator -----	From about 2 to 5
Pickling inhibitor -----	From about 1 to 2
Wetting agent or wetting agent mixture -----	From about 7 to 12
Solvent (water soluble) -----	From about 6 to 8
Water -----	From about 64 to 38

The inorganic acids contemplated are phosphoric and hydrochloric acids which are used together in the bath. Sulfuric or sulfamic acids may be optionally present. The presence of the later acids are advantageous where a heavier degree of rust is present on the article.

The pickling accelerator may comprise a substance from the group consisting of gluconic acid and its alkali salts, alkali fluoride (e.g. sodium fluoride), and alkali fluoroborates (e.g. sodium fluoroborate).

Inhibitors which are particularly advantageous in small but effective amounts when employed in the composition as corrosion inhibitors are: aldehydes, amines and nitriles, heterocyclic compounds, compounds in which the sulfur is bound up as mercaptan or sulfide sulfur, thiosemicarbazoles and similar compounds as customarily used as pickling inhibitors, such as 1,4-butyndiol, dibenzylsulfoxide, benzotrithion, 2-methyltrithion, 3-(p-methoxyphenyl)-trithion and the like.

The wetting agents employed may be anion-active, non-anionic and ampholytic detergents, including mixtures thereof, provided they have good wetting and emulsifying action and are capable of screening off the solutions of high hydrochloric acid content by means of a blanket of foam. Examples of such agents are primary and secondary alkyl sulfates, sulfates of oxo- and other branched alcohols, alkyl sulfonates of fatty acids and their esters, alkyl benzene sulfonates, alkyl naphthalene sulfonates, polyglycol ether, polyoxypropylene glycol, polyalkyl aryl glycol ethers, amides of alkyl sulfonic acids, betaine, sulfobetaine, and their substitution products. A wetting agent known in the trade as "Pluronic" (polyoxypropylene glycol) may be employed. An anion agent referred to in the trade as Benax 2A1 (sodium salt of dodecylated oxydibenzene disulfonate) may likewise be employed.

Organic solvents which may be advantageously used in carrying out the invention are those of a polar character which are substantially miscible in water and have good dissolving power for fats, fatty acid and mineral

oils. Examples of such solvents are butyl glycol, propyl glycol, ethyl polyglycol, methyl and ethyl ethers of ethylene and propylene glycol, methyl ethyl ketone and ethyl glycol acetate.

In case of moderate dirt or rust formation, the following composition is particularly useful:

	Percent by weight
Hydrogen chloride (100%) -----	From about 15 to 10
Orthophosphoric acid (100%) -----	From about 9 to 22
Sulfamic acid -----	From about 2 to 1
Sodium Borogluconate -----	From about 2 to 3
Wetting agent, sodium salt of dodecylated oxydibenzene disulfonate -----	From about 7 to 10
Solvent, propyl glycol -----	From about 6 to 8
Water, essentially the balance -----	From about 59 to 46

For only slightly rusted deep-drawn steel plates such as used, inter alia, in the automobile industry, the following composition is particularly preferred:

	Approximate percent by weight
Hydrogen chloride (100%) -----	10
Orthophosphoric acid (100%) -----	22
Sulfamic acid -----	1
Sodium borogluconate -----	3
Wetting agent, sodium salt of dodecylated oxydibenzene disulfonate -----	7
Solvent, propyl glycol -----	8
Water -----	49

In order to produce the particularly preferred product, about 32% by weight of hydrochloric acid (about 32%), and about 26% by weight of thermal phosphoric acid (about 85%) are first of all carefully introduced with continuous agitation into about 30% by weight tap water, whereupon slowly about 1% by weight sulfamic acid is added and then, after cooling, the above indicated quantities of sodium borogluconate, wetting agent and solvent are added, and the entire mixture then stirred until completely dissolved or mixed.

The workpieces are treated with this agent by manual application, dipping, spraying or atomizing. The time of action depends on the degree of contamination by drawing, as well as the amount of corrosion. In case of only slight dirtying or normal rusting (for instance a thin film of rust), it is sufficient to allow the agent to act for a few minutes at room temperature. In order to obtain a passivating layer, the workpieces are exposed beyond the period of time necessary for draining also for an additional 1 to 2 minutes to the action of the still adhering liquid film.

In the second method step, the solution of the first step is removed from the workpieces by thorough washing with normal tap water. By the application of pressure and/or heating the rinsing water to about 30° C., the water washing can be made more intensive and shortened in time. The drying by water displacement connected with the following step of the treatment makes unnecessary the drying by heat which was previously necessary after the water washing.

In the third method step, the wet workpieces are treated with a special solution by manual application, dipping or spraying. This product consists of a volatile non-polar solvent, a wetting agent or mixture of wetting agents, a small amount of solubilizer and a film-forming organic substance which, after evaporation of the solvent, will form a drying, corrosion-preventing film which can be baked. This film can also be baked together in one operation with one of the customary lacquer primings after the drying or hardening.

Such a solution may have the following composition:

	Percent by weight
Organic solvent -----	From about 92 to 71
Wetting agent or mixture of wetting agents -----	From about 1.0 to 1.8
Solubilizer -----	From about 0.4 to 1.0
Film-former -----	From about 6.5 to 26.0
Drying substance -----	From about 0.1 to 0.2

Organic solvents that can be used include medium- to high-boiling aliphatic and aromatic hydrocarbons. For industrial health reasons, however, aliphatic hydrocarbons such as white spirits having a boiling range of between 150 and 190° C. are preferred. In this connection, the range between initial point and end point of the boiling should be as small as possible, and not exceed 30° C. Furthermore, at least 99% by volume must distill over before the end point. Examples of white spirits that may be used are nonane (B.P. 150.6° C.), decane (B.P. 174° C.), undecane (B.P. 197° C.) or crude mixtures thereof. The mineral spirits used must be practically free of sulfur (less than 0.005% by weight), have a flash point of 39±1° C., density of about 0.776 (15° C.) and an evaporation number of 60. Examples of aromatic hydrocarbons are n-propylbenzene (B.P. 159.2° C.), p-methylisopropylbenzene (B.P. 176° C.), and the like. As stated hereinbefore, it is preferred for health reasons that the aliphatic hydrocarbons such as white spirits have a boiling range of between 150 and 190° C., the range between the initial point and the end point not exceeding 30° C.

With respect to the wetting agent or wetting agent mixture which imparts the water-displacing property to the solution, it must be readily soluble in aromatic or aliphatic hydrocarbon and difficultly soluble to insoluble in water and have strongly predominant hydrophobic properties. Such wetting agents are employed in small but effective amounts. Various groups of non-ionic wetting agents and their mixtures have proven to be particularly suitable, such as oxethylated octylphenols, oxethylated nonylphenols, octylphenoxy-polyethoxy-ethanol, and nonyl phenol polyglycol ethers.

As a solubilizer for the wetting agents, polar compounds can be used in small but effective amounts which are readily soluble in white spirits but scarcely soluble in water, and the boiling point of which lies below or within the boiling range of the solvent. Those found suitable for the purpose are: benzyl alcohol, octyl alcohol, cyclohexanone, methyl cyclohexanone, methyl cyclohexanol and cyclohexanolacetate.

With regard to the film-former, it has been found advantageous to use mixtures consisting predominantly of a varnish resin dried by oxidation and which is readily soluble in mineral spirits (white spirits). A varnish resin found useful is an oil-modified alkyd resin or mixtures of such varnish resins with slight additions of natural ceresin (paraffin wax) or saponified ceresins, neutral wool grease (lanolin), as well as a drying oil (linseed oil or wood oil).

Dryers which may be employed in small but effective amounts include resinates or naphthenates of cobalt, lead, manganese, zirconium and their mixtures.

In cases in which intermediate storage or transportation from plant to plant is not necessary, the following composition has proven satisfactory for giving film thicknesses of about 3 to 4 microns:

	Percent by weight
Linseed oil alkyd resin -----	From about 4.8 to 7.5
Saponified ceresin -----	From about 0.3 to 0.5
Lanolin (anhydrous) -----	From about 0.8 to 1.3
Wood oil -----	From about 0.4 to 0.6
Octylphenol polyglycol ether ..	From about 1.0 to 1.3
Benzyl alcohol -----	From about 0.35 to 0.75
Cobalt-naphthenate (5.5% Co) -----	About 0.05
Zirconium naphthenate (6.0% Zr) -----	About 0.1
White spirits (B.P. 150/180° C.) essentially the balance ---	From about 92.2 to 87.9

In cases where film thicknesses of 5 to 8 microns are necessary in view of the necessity or possibility of lengthy intermediate storage even under unfavorable climatic conditions or of transportation from plant to plant, the following composition is particularly preferred:

	Approximate percent by weight
Linseed oil alkyd resin -----	7.5
Castor oil alkyd resin -----	7.5
Saponified ceresin -----	1.0
Lanolin (anhydrous) -----	2.5
Wood oil -----	1.5
Octylphenol polyglycol ether -----	1.5
Benzyl alcohol -----	1.0
Cobalt naphthenate (5.5% Co) -----	0.1
Zirconium naphthenate (6.0% Zr) -----	0.1
White spirits (150/180° C.) -----	77.3

For the preparation of the particularly preferred product, the film-formers (alkyd resins, ceresin, lanolin [anhydrous] and wood oil) are dissolved with continuous agitation at about 40° C. in 50% by weight of white spirits. Thereupon the benzyl alcohol, the wetting agent, the two naphthenates and last of all the rest of the white spirits are added. The mixture is stirred until it has cooled down completely to room temperature and then filtered through a fine nylon screen.

The workpieces which have been pretreated in the first step and washed in the second step are treated with this agent by manual application or by dipping or spraying. In the case of dipping, the agent is allowed to act for a few minutes. Since the added wetting agent strongly reduces the surface tension of this solution, the water adhering to the workpieces is displaced from the surface. As a result of its specific gravity, the water drops to the bottom of the bath from where it is drained off from time to time. After the removal of the workpiece, it is allowed to drip for a short time. The air-drying or hardening is completed in about 45 to 60 minutes. The hardening can be accelerated by preheated circulating air.

While the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. A method of treating the surface of an iron-base metal article which comprises subjecting the surface of the article to the action of a pickling solution containing about 20% to 35% by weight of a mixture of phosphoric acid and hydrochloric acid; about 2% to 5% by weight of a pickling accelerator selected from the group consisting of gluconic acid and alkali salts thereof, alkali fluorides, and alkali fluoroborates; a small but effective amount of a pickling inhibitor selected from the group consisting of 1,4-butyndiol, dibenzylsulfoxide, benzotrithion, 2 - methyl - trithion, 3 - (p - methoxyphenyl)-trithion; about 7% to 12% by weight of at least one wetting agent selected from the group consisting of secondary alkyl sulfates, sulfates of oxo- and other branched alcohols, alkyl sulfonates of fatty acids and their esters, alkyl benzene sulfonates, alkyl naphthalene sulfonates, polyglycol ether, polyoxypropylene glycol, poly-alkyl aryl glycol ethers, amides of alkyl sulfonic acids, betaine, sulfobetaine and their substitution products, and a sodium salt of dodecylated oxydibenzene disulfonate; about 6% to 8% by weight of an organic solvent selected from the group consisting of butyl glycol, propyl glycol, ethyl polyglycol, methyl and ethyl ethers of ethylene and propylene glycol, methyl ethyl ketone and ethyl glycol acetate; and the balance essentially water from about 64% to 38% by weight; washing said article with water

after completion of pickling; and finally treating the washed surface with a solution containing a small but effective amount of at least one wetting agent selected from the group consisting of oxethylated octylphenols, oxethylated nonylphenols, octyl - phenoxy - polyethoxy-ethanol and nonyl phenol polyglycol ethers; a small but effective amount of solubilizer selected from the group consisting of benzyl alcohol, octyl alcohol, cyclohexane, methyl cyclohexane, methyl cyclohexanol and cyclohexanolacetate; about 6.5% to 26% by weight of a film-forming varnish resin readily soluble in mineral spirits comprising an oil-modified alkyd resin; a small but effective amount of a dryer selected from the group consisting of resinates and naphthenates of cobalt, lead, manganese, zirconium and mixtures thereof; and the balance essentially about 92% to 71% by weight of an organic solvent selected from the group consisting of aliphatic and aromatic hydrocarbons having a boil point ranging from about 150° to 180° C., whereby the finally treated surface is characterized by a corrosion-preventing film of varnish which may serve as a base for receiving a primer, enamel or other coating.

2. The method of claim 1 wherein the pickling solution comprises by weight of the following:

- about 15 to 10% hydrochloric acid;
- about 9 to 22% orthophosphoric acid;
- about 2 to 1% sulfamic acid;
- about 2 to 3% pickling accelerator;
- about 7 to 10% wetting agent;
- about 6 to 8% organic solvent;
- about 59 to 46% water as essentially the balance.

3. The method of claim 1 wherein the solution employed in the final treatment after washing the article with water comprises by weight:

- about 4.8 to 7.5% linseed oil alkyd resin;
- about 0.3 to 0.5% saponified ceresin;
- about 0.8 to 1.3% lanolin (anhydrous);
- about 0.4 to 0.6% wood oil;
- about 1.0 to 1.3% octylphenol polyglycol ether;
- about 0.35 to 0.75% benzyl alcohol;
- about 0.05% cobalt naphthenate;
- about 0.1% zirconium naphthenate;
- about 92.2 to 87.9% white spirits (B.P. 150/180° C.) as essentially the balance.

4. The method of claim 1 wherein the pickling solution comprises by weight:

- about 10% hydrochloric acid;
- about 22% orthophosphoric acid;
- about 1% sulfamic acid;
- about 3% sodium borogluconate;
- about 7% of the sodium salt of dodecylated oxydibenzene disulfonate;
- about 8% of propylglycol;
- about 49% water as essentially the balance;

and wherein the solution employed in the final treatment after washing the article comprises by weight:

- about 7.5% linseed oil alkyd resin;
- about 7.5% castor oil alkyd resin;
- about 1.0% saponified ceresin;
- about 2.5% lanolin (anhydrous);
- about 1.5% wood oil;
- about 1.5% octyl polyglycol ether;
- about 1.0% benzyl alcohol;
- about 0.1% cobalt naphthenate;
- about 0.1% zirconium naphthenate;
- about 77.3% white spirits (150/180° C.) as essentially the balance.

5. The method of claim 1, wherein the acid mixture also includes an acid selected from the group consisting of sulfuric acid and sulfamic acid.

6. A method of treating the surface of iron-base metal articles such as steels, in which metal surfaces are pickled in a pickling bath in a first step, rinsed with water in a second step and provided with a protective coating in a third step, which comprises subjecting

said articles to a pickling bath having the following composition:

- (a) about 20–35% by weight of a mineral acid mixture (calculated on 100% acid) of phosphoric and hydrochloric,
- (b) about 2–5% by weight of a pickling accelerator selected from the group consisting of gluconic acid and alkali salts thereof, alkaliborogluconates, alkali fluorides and alkali fluoroborates,
- (c) about 1–2% by weight of a corrosion inhibitor selected from the group consisting of aldehydes, amines, nitriles, heterocyclic compounds, compounds in which the sulfur is bound up as mercaptan or sulfide sulfur and thiosemicarbazoles,
- (d) about 7–12% by weight of a wetting agent selected from the group comprising anion active, non-anionic and ampholytic detergents having good wetting and emulsifying action,
- (e) about 6–8% by weight of a solvent of a polar character which is miscible in water and serves as a solvent for fats, fatty acids and mineral oils, and
- (f) about 38–64% by weight of water, rinsing said articles and then applying a protective coating using the following composition:
- (g) about 71–92% by weight of an organic solvent selected from the group consisting of medium and high boiling aliphatic and aromatic hydrocarbons,
- (h) about 1–1.8% by weight of a wetting agent which is easily soluble in the organic solvent and has hydrophobic properties and is not ionic, including about .4 to 1% by weight of a solubilizer, the boiling point of which lies within or below the boiling range of the organic solvent,
- (i) about 6.5–26% by weight of a film-former of a varnish resin which is readily soluble in mineral spirits (white spirits) and which dries by oxidation, such as an oil-modified alkyd resin or mixtures of such resins with additions selected from the group consisting of natural ceresin, saponified ceresin, neutral wool grease, including a drying oil, and
- (j) about .1–.2% by weight of a drying substance,

whereby a corrosion-protective film is formed on the articles as a basic layer for a priming paint, varnish or other coatings.

7. The method of claim 6, wherein the acid mixture also includes an acid selected from the group consisting of sulfuric acid and sulfamic acid.

8. A method of treating the surface of an iron-base metal article which comprises, subjecting the surface of the article to the action of a pickling solution containing about 20% to 35% by weight of an acid selected from the group consisting of phosphoric acid and hydrochloric acid and an acid from the group consisting of sulfuric and sulfamic acid; about 2% to 5% by weight of a pickling accelerator selected from the group consisting of gluconic acid and alkali salts thereof, alkali fluorides, and alkali fluoroborates; a small but effective

amount of a pickling inhibitor selected from the group consisting of 1,4-butyndiol, dibenzylsulfoxide, benzotrithion, 2-methyl-trithion, 3-(p-methoxyphenyl)-trithion; about 7% to 12% by weight of at least one wetting agent selected from the group consisting of secondary alkyl sulfates, sulfates of oxo- and other branched alcohols, alkyl sulfonates of fatty acids and their esters, alkyl benzene sulfonates, alkyl naphthalene sulfonates, polyglycol ether, polyoxypropylene glycol, polyalkyl aryl glycol ethers, amides of alkyl sulfonic acids, betaine, sulfobetaine and their substitution products, and a sodium salt of dodecylated oxydibenzene disulfonate; about 6% to 8% by weight of an organic solvent selected from the group consisting of butyl glycol, propyl glycol, ethyl polyglycol, methyl and ethyl ethers of ethylene and propylene glycol, methyl ethyl ketone and ethyl glycol acetate; and the balance essentially water from about 64% to 38% by weight; washing said article with water after completion of pickling; and finally treating the washed surface with a solution containing a small but effective amount of at least one wetting agent selected from the group consisting of oxethylated octylphenols, oxethylated nonylphenols, octyl-phenoxy-polyethoxy-ethanol and nonyl phenol polyglycol ethers; a small but effective amount of solubilizer selected from the group consisting of benzyl alcohol, octyl alcohol, cyclohexane, methyl cyclohexane, methyl cyclohexanol and cyclohexanolacetate; about 6.5% to 26% by weight of a film-forming varnish resin readily soluble in mineral spirits comprising an oil-modified alkyd resin; a small but effective amount of a dryer selected from the group consisting of resinates and naphthenates of cobalt, lead, manganese, zirconium and mixtures thereof; and the balance essentially about 92% to 71% by weight of an organic solvent selected from the group consisting of aliphatic and aromatic hydrocarbons having a boil point ranging from about 150° to 180° C., whereby the finally treated surface is characterized by a corrosion-preventing film of varnish which may serve as a base for receiving a primer, enamel or other coating.

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U.S. Cl. X.R.

117—75, 132; 134—41; 252—79.4